THESES

IDENTIFICATION OF MAGNETIC MINERALS IN THE FINE-GRAINED SEDIMENTS OF LAKE PANNON WITH MAGNETIC METHODS. PALAEOENVIRONMENTAL AND MAGNETOSTRATIGRAPHIC IMPORTANCE OF WIDESPREAD OCCURRENCE OF GREIGITE

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Budapest, 2008

Introduction

During the last decade Cenozoic sediments of the Carpathian Basin, such as deposits of former Lake Pannon were in the focus of interest of palaeomagnetic studies, therefore their magnetic minerals were also subjects of research. Mineralogical studies showed that the fine-grained sediments of Lake Pannon contain pyrite. Magnetostratigraphic studies of some cores suggested that the carrier of the remanence is primary magnetite, because pyrite is a paramagnetic mineral. However, recent palaeomagnetic studies showed that greigite, which can form during early- to late diagenesis, was the carrier of magnetic remanence in the sediments of Lake Pannon. This observation raised the question that what kind of magnetic minerals are found in the fine-grained sediments of Lake Pannon, and which one carries the palaeomagnetic/magnetostratigraphic signal.

The identification of greigite by mineralogical studies in sediments is difficult. Nevertheless, systematically applied magnetic methods can be successful even if the concentration of greigite is very low. Oriented and unaltered samples are suitable for palaeomagnetic studies, therefore the aim of my PhD work was to perform palaeomagnetic and rock magnetic measurements of fresh samples from outcrops and to interpret data. In addition, samples which had been measured earlier for palaeomagnetics, were also studied by detailed rock magnetic measurements.

The magnetic method also permits to estimate the age of formation of the magnetic minerals, relative to the age of deposition of the sediments. Sediments in which magnetization occurred short time after the sedimentation are suitable for magnetostratigraphic studies. The magnetic minerals which formed during sedimentation or during very early diagenesis indicate oxygenation of the palaeoenvironment, because magnetic iron-sulphides indicate reductive environments.

Applied methods

Magnetic mineralogy experiments are often carried out on unoriented samples, however our samples were taken for palaeomagnetic analyses oriented in situ with a magnetic compass, about 10 from each locality. Secondary minerals can be filtered by palaeomagnetic investigations, because these minerals do not carry a consistent palaeomagnetic signal. The investigated samples represent mostly dark-grey, typically fine-grained, visibly unaltered sediments. The samples were stored in a refrigerator, isolated from air and were rapidly processed.

Magnetic experiments were carried out in two ways: the carrier of the natural remanence was investigated during the measurements of natural remanent magnetization (NRM), however all the magnetic minerals were examined during the measurements of isothermal remanent magnetization (IRM). Comparison between the NRM and IRM behaviour on heating indicates that the actual and potential carriers of the remanence in the same sample were the same.

In the course of the experiments, the NRM intensity and low-field magnetic susceptibility were measured in natural state. One specimen per sample was subjected to demagnetization, while the other specimen (kept in a refrigerator) was re-measured in the natural state from time to time, providing the possibility to monitor what happens between sampling and first measurements. Thermal and alternating field demagnetization was followed by consistency analysis, which showed the time of formation of magnetic minerals.

Laboratory analysis of the NRM was followed by special rock magnetic experiments (acquisition of IRM, stepwise thermal demagnetization of a three-component IRM, test to distinguish between greigite and pyrrhotite, low-temperature experiments). Results from these experiments showed what kind of magnetic minerals are found in the samples. Hysteresis loops suggested the domain state and mass percent of magnetic minerals.

I wanted to document the presence of greigite in the fine-grained sediments of Lake Pannon by mineralogical methods, too. Although extracts of sufficient quantity did not show the presence of greigite; it was identified by Mössbauer-spectroscopy without extract.

Theses

1. My systematically applied magnetic measurements showed that in the fine-grained sediments of Lake Pannon greigite occurs widespread (in 17 localities alone, in two cases with magnetite), magnetite was identified at 13 localities, generally with pyrite, haematite was found at three localities and pyrrhotite occurs only subordinately (at one locality with greigite).

2. During identification of the magnetic minerals, the minerals had different behaviours than it was accepted:

a, I documented that the rapid decrease of NRM intensity and susceptibility of greigite-bearing sediments after sampling was not likely to be connected to greigite, but rather is the result of decomposition of hydrated iron sulphates.

b, My measurements supported that the rapid screening of NRM/IRM intensity and susceptibility is not sufficient for the identification of magnetic minerals.

c, The intensity of some greigite-bearing samples decreased to zero by 360°C (in accordance with data of classical papers), but often the complete loss of NRM intensity was at 410°C.

d, The typical susceptibility decrease (between 200–400°C) of greigite-bearing sediments was not observable in several cases. During thermal demagnetization the susceptibility did not behave in a uniform way in samples collected from the same locations.

e, During the test distinguished between greigite and pyrrhotite, in the greigite-bearing sediments the minima suggested the main phase transitions. The first minimum was at 200°C in samples of Lake Pannon and in the original experiments (Torii et al. 1996), too. However this minimum was not likely to be connected to greigite, but rather smythite (Krs et al. 1992). In contrast to the original experiments, where one minimum was at 300°C, in samples of Lake Pannon there were two, one at 275°C and one at 320°C.

c, and d, points were supported by results of Pósfai et al. (2001).

3. The results of hysteresis measurements showed that the amount of greigite is very low (<<1%) in these sediments. Greigite has small grain size and often hides in framboidal pyrites therefore its identification in sediments of Lake Pannon by mineralogical methods was not successful. Nevertheless, I identified it by Mössbauer-spectroscopy.

4. During special rock magnetic measurements all the magnetic minerals are examined, but during the palaeomagnetic and magnetostratigraphic investigations the carrier of the natural

remanence is important only. The consistency analysis shows that the measured NRM is a primary or a secondary origin. My investigations show:

a, Sediments, in which greigite carries the NRM have good statistical parameters, got their remanent magnetization in a short time, during very early stage of diagenesis. Therefore they are suitable for tectonic interpretation and for magnetostratigraphic correlation as well.

b, The magnetite-bearing sediments got their remanent magnetization over longer time period, their magnetization is probably secondary.

c, When greigite and magnetite carry together the NRM, the remanent magnetization of the two minerals has got opposite polarities, either greigite or magnetite (or both) must have a late origin, but it is impossible to say which one.

5. The diagenetic origin of the widespread greigite, as well as the possibility of neoformation of greigite and other magnetic minerals suggest that palaeomagnetic and magnetostratigraphic investigations of Lake Pannon sediments must be carried out on fully oriented cores, and should be accompanied by detailed mineral magnetic studies in order to avoid pitfalls in interpretation of palaeomagnetic data. As I have shown, documentation of consistency is also essential when magnetite is the dominant magnetic mineral, because this mineral can also have a secondary origin.

6. The relationship of magnetic minerals of the fine-grained sediments of Lake Pannon and the environment (Table 1):

a, Oldest (11–8.5 Ma) sediments were deposited below storm wave base. In sediments, which have good or excellent palaeomagnetic signal, greigite carries the signal, magnetite-bearing sediments do not carry a coherent palaeomagnetic signal. Large rivers carried fresh water to the lake, which could not immediately mix with saline water, therefore the water column was stratified, and the bottom waters were oxygen-depleted. Such condition favoured greigite formation. Preservation of this mineral was secured by rapid burial due to the large sedimentary input from the surrounding mountain chains.

b, In sediments formed in the 8.5–6.5 Ma period, only greigite occurs and carries a good palaeomagnetic signal.

c, The youngest studied sediments (6.5–4 Ma) were deposited in different environments and have different magnetic minerals. In this group of localities, the dominant carrier of the statistically well-defined NRM is magnetite, especially when deposition was in distal environments (when burial was slow). Nevertheless, greigite and haematite also occur, greigite occurs in lake sediments, and haematite occurs in floodplain deposits.

7. The widespread occurrence of greigite in the fine-grained sediments of Lake Pannon show, that the sedimentary environment was reductive during the early stage of diagenesis, but it is possible, that the bottom water might have been similar. These oxygen-depleted environments formed in relatively small water depth, already on the delta plain, as a result of some local effects.

	Locality	Age (Ma)	Environment	Magnetic mineral	Palaeomagnetic signal
3	Mályi (H)	11–8.5	sublittoral, below storm wave base; proximal deposition; water depth: a few 10s of metres	greigite	excellent
4	Sopron (H)	11–8.5	sublittoral, below storm wave base; proximal deposition; water depth: a few 10s of metres	greigite	excellent
5	Pannonhalma (H)	11–8.5		magnetite	bad
6	Kisbér (H)	11–8.5	sublittoral, below storm wave base; proximal deposition; water depth: several 10s of metres	greigite	good
7	Tata (H)	11–8.5	sublittoral, below storm wave base; proximal deposition; water depth: several 10s of metres	greigite	excellent
8	Bakonyszentlászló (H)	11–8.5	sublittoral, below storm wave base; proximal deposition; water depth: a few 10s of metres	greigite	good
9	Várpalota (H)	11–8.5		greigite (?)	good
10	Székesfehérvár (H)	11–8.5	mostly redeposited sediment	magnetite	bad
11	Devecser (H)	11–8.5	sublittoral, below storm wave base; proximal deposition; water depth: several 10s of metres	greigite	good
12	Raposka (H)	11–8.5	sublittoral, below storm wave base; proximal deposition; water depth: a few 10s of metres	magnetite	bad
1	Gyöngyösvisonta (H)	8.5–6.5	shallow interdistributary bay to floodplain	greigite (?)	bad
2	Bükkábrány (H)	8.5–6.5	shallow interdistributary bay to floodplain, low salinity or fresh water	greigite	good
14	Marótpuszta (H)	8.5–6.5	upper delta plain; very shallow lacustrine to floodplain, low salinity or fresh water	greigite	good
15	Kakasd (H)	8.5–6.5	sublittoral, below storm wave base; proximal deposition; water depth: several 10s of metres	greigite	good
16	Bátaszék (H)	8.5–6.5	sublittoral, below storm wave base; proximal deposition; water depth: a few 10s of metres	greigite	excellent
17	Trdkova (SLO)	6.5–4		haematite	good
18	Gornji Petrovci (SLO)	6.5–4	flood-plane deposit, low salinity or fresh water	haematite	bad
19	Miklavž pri Ormožu (SLO)	6.5–4		greigite	excellent
20	Pince (SLO)	6.5–4	brackish water of low salinity	haematite	good

Table 1. The carrier of the palaeomagnetic/magnetostratigraphic signal and the reliability of this signal in different environment of Lake Pannon.

Locality	Age (Ma)	Environment	Magnetic mineral	Palaeomagnetic signal
21 Hum Zabočki (HR)	6.5–4	sublittoral, below storm wave base; proximal deposition; water depth: a few 10s of metres	greigite	good
22 Podgorci (SLO)	6.5–4		pyrrhotite (+ greigite)	good
23 Mirti (HR)	6.5–4	open lake, brackish water of low salinity, low terrigenous input; distal deposition; water depth: few 100s of metres	magnetite (+ pyrite)	excellent
24 Samci (HR)	6.5–4	open lake, brackish water of low salinity, low terrigenous input; distal deposition; water depth: few 100s of metres	magnetite	good
25 Molvice (HR)	6.5–4	open lake, brackish water of low salinity, low terrigenous input; distal deposition; water depth: few 100s of metres	magnetite (+ pyrite)	excellent
26 Podsused (HR)	6.5–4	open lake, brackish water of low salinity, very low terrigenous input; distal deposition; water depth: max. 50 m	magnetite (+ pyrite)	good
27 Slanovec (HR)	6.5–4	open lake, brackish water of low salinity, very low terrigenous input; distal deposition; water depth: max. 50 m	greigite	good
28 Medvedski Breg (HR)	6.5–4	open lake, brackish water of low salinity, very low terrigenous input; distal deposition; water depth: max. 50 m	magnetite (?)	good
29 Novoselci (HR)	6.5–4	prodelta, brackish water of low salinity, medium to high terrigenous input; proximal-distal deposition; hypoxic conditions; water depth: few 100s of metres	greigite	good
30 Dol (HR)	6.5–4	open lake, brackish water of low salinity, very low terrigenous input; distal deposition; water depth: max. 50 m	magnetite (+ pyrite)	good
31 Požeški Pavlovci (HR)	6.5–4	open lake, brackish water of low salinity, low terrigenous input; distal deposition; water depth: few 100s of metres	magnetite	good
32 Grižiči (HR)	6.5–4	open lake, brackish water of low salinity, very low terrigenous input; distal deposition; water depth: max. 50 m	magnetite (?)	good
33 Beočin (SRB)	6.5–4		magnetite (+ pyrite)	bad
34 Remetice (SRB)	6.5–4		greigite	good
13 Pula (H)	6.5–4	crater lake	greigite (?)	good
I Monostorpályi (H)			magnetite?	
II Diósberény (H)			greigite + magnetite	opposite
III Udvari (H)			greigite + magnetite	opposite

Table 1. – continued.

References

Krs, M., Novak, F., Krsova, M., Pruner, P., Koulikova, L. & Jansa, J. 1992: Magnetic properties and metastability of greigite–smythite mineralization in brown-coal basins of the Krusne hory, Piedmont, Bohemia. – *Phys. Earth Planet. Inter.* **70**, 273–287.

Pósfai, M., Cziner, K., Márton, E., Márton, P., Buseck, P.R., Frankel, R.B. & Bazylinski, D.A. 2001: Crystal-size distributions and possible biogenic origin of Fe sulfides. – *Eur. J. Mineral.* **13**, 691–703.

Torii, M., Fukuma, K., Horng, C.–S. & Lee, T.–Q. 1996: Magnetic discrimination of pyrrhotite- and greigite-bearing sediment samples. – *Geophys. Res. Lett.* **23**, 1813–1816.

List of publications

Referred scientific papers

Márton P., Mártonné Szalay E., **Babinszki E.** & Kiss L.F. 2006: Környezeti hatások kutatása a vasszulfid-tartalmú üledékes kőzetek mágneses tulajdonságai alapján. (Study of the environmental effects using magnetic characteristics of sedimentary rocks with Fe-sulphides.) – *Magyar Geofizika* **47/4**, 183–186 (in Hungarian with English abstract).

Babinszki, E., Márton, E., Márton, P. & Kiss, L.F. 2007: Widespread occurrence of greigite in the sediments of Lake Pannon: Implications for environment and magnetostratigraphy. – *Palaeogeography, Palaeoclimatology, Palaeoecology* **252**, 626–636.

Babinszki E. & Mártonné Szalay E. (in preparation): A greigit, mint a paleomágneses jel hordozójának azonosítása mágneses módszerekkel, a Pannon-tó üledékeiben. (Identification of greigite in the sediments of Lake Pannon as the carrier of the palaeomagnetic signal with magnetic methods) – *Földtani Közlöny* (in Hungarian with English abstract).

Conference abstracts

Márton, E., Márton, P., **Babinszki, E.** & Kiss, L.F. 2002: Environment and greigite formation: Suboxic conditions in the miocene Fore-Carpathian Depression and in Lake Pannon. – *8th Castle Meeting. Paleo, Rock and Environmental Magnetism, Castle of Zahrádky, Czech Republic, September 2–7, 2002,* Abstract Volume.

Babinszki E. 2003: A mágneses paraméterek változása a környezeti tényezők függvényében, a Pannon-tó üledékeiben. – *Ifjú Szakemberek Ankétja, Dobogókő, 2003. március 21–22.,* Absztrakt kötet, p. 57–58.

Babinszki, E., Márton, E., Márton, P. & Kiss., L.F. 2004: Magnetic identification of the magnetic mineral greigite in fine-grained sediments of Lake Pannon. – *2nd Mid-European Clay Conference, Miskolc*, *Hungary, September 20–24, 2004,* ACTA Mineralogica-Petrographica Abstract Series Vol. 4, p. 9.

Babinszki, E., Márton, E., Márton, P. & Kiss, L.F. 2006: Widespread occurrence of greigite in the fine-grained sediments of Lake Pannon: Implications for environment and magnetostratigraphy. – *3rd „Mineral Sciences in the Carpathians" International Conference, Miskolc, Hungary, March 9–10, 2006,* ACTA Mineralogica–Petrographica Abstract Series Vol. 5, p. 6.

Oral presentations (in Hungarian)

Babinszki E., Mártonné Szalay E., Márton P. & Kiss L.F. 2004: A Pannon-tó mágneses ásványainak azonosítása mágneses módszerekkel, különös tekintettel a vas-szulfidokra. – *A Magyar Geofizikusok Egyesülete, az MFT Általános Földtani és Ásványtan–geokémiai Szakosztályainak előadóülése, Budapest, 2004. március 22.*

Babinszki E., Mártonné Szalay E., Márton P. & Kiss L.F. 2006: A greigit mágneses azonosításának menetrendje. – *Az MTA Geokémiai és Ásvány–kőzettani Tudományos Bizottsága Nanoásványtani Munkabizottságának és az MFT Ásványtan–geokémiai Szakosztályának Nanoásványtani Ankétja, Balatonfüred, 2006. január 19–20.*

Márton P., Márton E., **Babinszki E.** & Kiss L.F. 2007: Környezeti hatások kutatása a vasszulfid-tartalmú üledékes kőzetek mágneses tulajdonságai alapján. – *Geofizikai OTKA projektek IV. seregszemléje, Budapest, 2007. január 15.*